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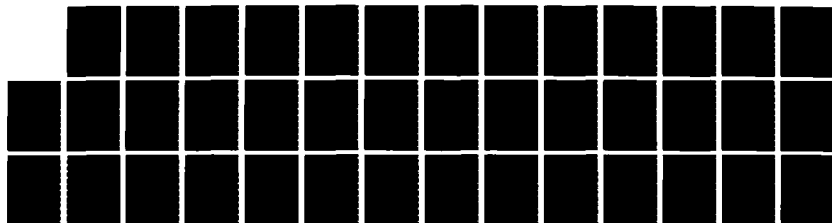
PHYSICAL PROPERTIES AND STRUCTURE OF ION-CONTAINING
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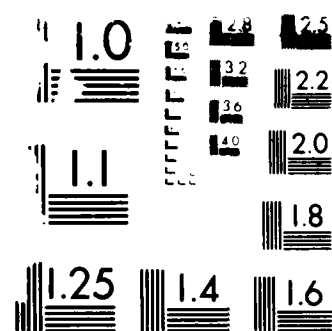
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Physical Properties and Structure of Ion-Containing Polymers

Final Report

Submitted by Dr. A. Eisenberg

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The progress made under this contract during the past three years, 1983 to the present, will be presented in 4 sections, i.e. blends, block copolymers, structure-property relations, and membranes. The largest of these is the section dealing with blends. This section includes the work done on miscibility enhancement using ion-ion or ion-dipole interactions in simple copolymers as well as the polyurethanes. Preliminary studies of systems based on highly incompatible materials (such as hydrocarbons and fluorocarbons) will also be included. The next section describes the synthesis and mechanical property studies of the block copolymers containing short ionic end blocks. The section dealing with structure-property relations covers a wide range of studies ranging from the introduction of hitherto unexplored ion types (such as phenoxy) into polystyrene to preliminary studies of ionic "combs" and melt rheology investigations of ionomer-diluent systems. The last section gives a very brief description of a study of a membrane material based on aromatic ionomers.

A. Blends

The study of blends of sulfonated polystyrene (PS) with ethyl acrylate-4 vinyl pyridine (EA-4VP) copolymers has been completed (1,2). It was shown that even at a 4% functional

group content the samples were homogeneous, with ca. 80% of the 4VP units being quaternized. Preliminary attempts were also made to determine the ΔH of the reaction on model systems in various solvents, with ΔH_m values falling into the range of 20-60 kJ/mol, depending on the detailed conditions.

The mechanical property studies showed behavior typical of one-phase systems if the functional group content was $\geq 4\%$, while concentrations below that value gave results typical of heterogeneous materials. The dynamic melt properties of these blends were also investigated (3). Measurements of dynamic shear moduli as a function of frequency at various temperatures above the glass transition indicate that time-temperature superposition is applicable in almost all cases. Relative to a blend of pure polystyrene with pure poly(ethyl acrylate), the copolymer blends strongly resemble one another. The blend of 2 mol % ion content resembles those of higher ion contents even though it is incompatible. The ionic interactions result in a greatly extended rubberlike plateau that decreases very slowly. Greater ion content appears to enhance the extension of the rubbery plateau. True flow is not achieved even at temperatures as high as 220°C (0.1 rad/s). Flow is

clearly evident in the nonionic blend at 170°C (0.1-1.0 rad/s). It is postulated that the ionic interactions are such that bond breaking and reforming are more rapid than the rate of chain slippage.

The study of the homoblends (mixtures of sulfonated PS with PS-4VP copolymers) was also completed (1). This study was performed to explore the nature of the ionic "cross-links" in the materials. Again, extensive proton transfer was observed, the shapes of the modulus vs temperature curves being very similar to those of pure polystyrene. The modulus range of 10^9 to 2×10^2 N/m² was covered by a combination of stress relaxation and dynamic mechanical techniques. This study shows that the cross-links are highly thermolabile and that normal injection molding techniques probably will be satisfactory for blends of this type, although at slightly higher temperatures than for pure polystyrene.

Blends were also prepared of sulfonated PS with various low molecular weight amines (1). Flexible alkyl amines depress the glass transition temperature, the depression being as high as 55° for tri-n-octylamine in the PS sulfonated to 8.1%. The depression is linear with chain length of the amine. Rigid amines, on the other hand, raise

the glass transition; for example, 1-adamantamine yields an increase of 12°. The modulus temperature curves show a strong resemblance to those of pure polystyrene. In the absence of ionic interactions, the C₂₄ amine yields a heterogeneous system, while their presence renders the material homogeneous.

Vinyl pyridine is a weak base. To explore the effect of stronger bases, an attempt was made to synthesize p-dimethylamino styrene. This attempt was successful. Also, these monomers can be copolymerized with styrene and probably other monomers as well.

Polyurethane blends were another area to receive considerable attention (4-11). The motivation for the study was to explore what happens to a segmented polyurethane (on the verge of phase separation) when a material is added which is miscible with only one of the components of the polyurethane. Also, it seemed desirable to explore systems in which an inexpensive material (a vinyl copolymer) could be used as an additive to an expensive matrix (the polyurethane). For this reason, blends of lightly sulfonated polystyrenes were prepared with polyurethanes containing a tertiary amine in the chain extender. In the absence of polystyrene, the polyurethanes are not phase

separated. Addition of the sulfonated polystyrene leads to a blend of the latter with the hard segments in one phase with the exclusion of the soft segments into a separate phase. The degree of phase purity of the soft segments increases with increasing sulfonate content at a constant styrene concentration, or with increasing styrene content at a constant sulfonate concentration in the styrene. Blend formation is confirmed in a study involving the mixing of a polyurethane containing hard segments without any soft segments, which lead to a one-phase system at a high enough sulfonated polystyrene content. The early phases of this work were already described in the final report for the preceeding contract. Several new aspects, however, were added.

FTIR studies of these blends confirm the proton transfer mechanism. A new absorption band at 3428 cm^{-1} corresponds to a stretching vibration of an $\text{N}^+\text{-H}$ bond. The 1012 cm^{-1} band of the SO_3H group, which strongly depends on the degree of protonation, shifts to lower frequency. The symmetric stretching vibration of the SO_3^- group, which occurred at 1043 cm^{-1} , shifts to lower frequency as well, suggesting a lower polarization of the S-O dipole due to the removal of H^+ .

One- and two-dimensional proton NMR spectra of blends of a polyurethane (PU) and poly(styrene - co - styrene sulfonic acid) (poly(S-co-SSA)) were analysed to determine the mechanism of interaction between the two components of the blend. A sample of poly(S-co-SSA) containing 7.9 mole % SSA was used, and the blends contained 58% poly(S-co-SSA). In DMSO solution, the labile protons of the SSA groups were transferred to the tertiary nitrogen of the N-methyl diethanolamine (MDEA) chain extender of the hard segment of the PU and to the urethane, allophanate and other secondary structures. Model compound studies and a 2D-COSY pulse sequence were used to make the assignments in the spectra. The labile proton was transferred preferentially to the secondary structures, followed by the urethane nitrogen, and then by the tertiary nitrogen of the MDEA.

In a subsequent study, blends were prepared from two kinds of urethane elastomers, containing 1,4-butanediol or 3,3'-dichloro-4,4'-diamino-diphenyl-methane as chain extenders, with lightly sulfonated polystyrenes. Dynamic mechanical studies show that strong interactions occur between the sulfonic acid and the urethane or urea moieties on the polyurethane chains. These strong interactions are clearly seen in the composition dependence of the loss

tangent peaks (due to the glass transitions) for both the high temperature and the low temperature glass transitions of the blends. They are further confirmed by model studies. Thus, it is seen that the sulfonic acid is a strong enough acid to transfer the proton to the urethane moiety, and that no amine is needed.

Recently, it was shown that ion pair-ion pair interactions can also be utilized to achieve miscibility in blends of urethanes with styrene ionomers. The urethanes contain quaternary ammonium salts in the hard segments, while the styrenes contain sodium methacrylate groups (~9.6 mol %). By contrast, ion-dipole interactions are not strong enough to achieve miscibility enhancement; a polyurethane containing short (ethylene oxide) sequences in the hard segment did not exhibit miscibility with a styrene-lithium methacrylate copolymer.

By contrast, in a very recent study, it was shown that if the polyether sequences are long enough, miscibility can be achieved via ion-dipole interactions. However, some of the hard segments of the polyurethane are also incorporated into the styrene-rich phase.

Mixing of a polyurethane (PU) with relatively short soft segments with a chlorinated polyisobutylene (ClPIB)

were also studied using dynamic mechanical measurements and ^1H - NMR spectroscopy. Two reactions can take place in the process of mixing. First, there is a dehydrohalogenation involving mainly the terminal chlorine of ClPIB and accelerated by annealing at high temperatures. The formed HCl reacts with the PU nitrogens generating positive charges on the PU chain. Second, there is an interaction between the PU nitrogens and the chloromethyl groups of the ClPIB side chains that also generates ionic groups. One- and two-dimensional (COSY) NMR spectra confirmed the proposed reactions. The resulting material was phase separated, with ClPIB being intimately mixed with the ion-containing hard segment of PU, and the soft segment of the PU forming a separated phase.

The investigation of the role of ion-dipole interactions in miscibility enhancement has continued in other areas as well.

The polystyrene-poly(alkylene oxide) system continued to receive attention (12,13). From the study of LCST behavior, it is shown that ion-dipole interactions can lead to truly thermodynamic miscibility in immiscible polymers. Blends of polystyrene (PS) ionomer with poly(propylene oxide) (PPrO) at low PPrO content undergo phase separation

upon heating and recover their transparency upon cooling. The miscibility enhancement (or the strength of the interaction) can be compared by comparing the position of the cloud point curves. An increase in the ion content of the PS ionomer shifts the cloud point curve to higher temperatures. A decrease in the counterion size in the PS ionomer (i.e., $K > Na > Li$) also increases the interaction, and leads to an upward shift of the cloud point curves. The effect of molecular weight is similar to that seen in non-ionic blends. The phase separation is a relatively fast process in a blend of a 10.4 mol % lithium methacrylate copolymer of styrene (S-0.104MAA-Li) mixed with PPrO and is completely reversible; a decrease in the ion content or an increase in the ionic radius of the counterions slows down the phase separation process, leading to only incomplete recovery of transparency upon cooling. This suggests that the lower the miscibility, the slower the phase separation process.

A wide range of other polar polymers were also investigated in a cursory fashion, the results being summarized in Table 1 (14).

Blends of poly(ethylene imine) were of particular interest since they exhibited complete miscibility. Two

ion-dipole systems were selected for a more thorough investigation, i.e. poly(ethyl acrylate) (PEA) ionomers/poly(ethylene imine) (PEI) and poly styrene ionomer/poly(ethylene imine). The poly(ethyl acrylate) ionomers were prepared by partial hydrolysis of PEA.

Copolymers of ethyl acrylate (EA) with lithium acrylate (LiA) with relatively low contents of LiA units (up to 30% were synthesized by alkaline hydrolysis of poly(EA). ^{13}C -NMR spectra of these copolymers registered in a mixture of deuterated benzene with deuterated methanol (85/15 v/v) presented configurational splittings of the ester methylene, methylene main chain and ester carbonyl group signals. Assignments of these splittings were made and Bernoulli statistics with a meso probability of 0.48 could fit both poly(EA) and poly(EA-co-LiA). Only the C=O signal of the copolymer was sensitive to sequence distribution and indicated that the LiA units have a tendency to be isolated on the chain. Two-dimensional HETCOR pulse sequence helped to assign the main chain proton spectrum (15).

TABLE 1

Ionomer	Polar Polymer	Chain Structure	Solvent	Preparative Method	Peak Shift	
					Pure Polymer	Ionomer
S-0.066MAA-Li	PVAc		Ben/MeOH(90/10)	freeze-drying	X	X
S-0.066MAA-Li	PDMS		Ben/MeOH(90/10)	freeze-drying	X	X
S-0.066MAA-Li	PCL		THF/MeOH(90/10)	precipitation	X	Δ
S-0.066MAA-Li	PVC		THF/MeOH(90/10)	precipitation	X	O
EA-0.18AA-Li	PEI		DMF/H2O(90/10)	evaporation	X	O
S-0.066MAA-Li	PET		m-cresol/MeOH(90/10)	evaporation	X	Δ
S-0.066MAA-Li	PECH		Ben/MeOH(90/10)	freeze-drying	X	Δ
S-0.066MAA-Li	PES		THF/MeOH(90/10)	precipitation	X	Δ
S-0.066MAA-Li	PSu		Ben/MeOH(90/10)	freeze-drying	X	Δ

X no shift of peaks
 Δ shift of peaks
 O single peak

Table 1

Abbreviations and symbols

PCL	=	Poly(caprolactone)
PEA	=	Poly(ethyl acrylate)
PECH	=	Poly(epichlorohydrin)
PEI	=	Poly(ethyleneimine)
PEO	=	Poly(ethylene oxide)
PES	=	Poly(ethylene succinate)
PET	=	Poly(ethylene terephthalate)
PPrO	=	Poly(propylene oxide)
PS	=	Polystyrene
PSu	=	Polysulfide
PVAc	=	Poly(vinyl acetate)
PVC	=	Poly(vinyl chloride)
X	=	Immiscible
△	=	Partly miscible
O	=	Homogeneous

Blends were prepared by solution blending. Each component was dissolved in DMF/water 90/10 v/v, the solutions mixed and a film obtained by evaporation in a vacuum oven and drying at 70°C. Samples containing from 10 to 50 wt % PEI were prepared. Most of the films were transparent. DMA of the blends showed that the matrix peak of the ionomer is not affected by the presence of the PEI while the cluster peak is shifted to lower temperatures by about 1.2°C per wt. percent PEI. In some samples it was possible to detect a PEI rich phase by DMA. In these samples the shift of the cluster peak was less than 1.2°C and the samples were opaque.

The above results suggest that PEI is miscible with the ionomers, while it is not with pure PEA. The blends seem to be composed of three phases: the matrix of the ionomer, the clusters and as much PEI as they can accomodate, and, in some samples of low ion contents or high PEI contents, of a phase consisting of residual PEI. For the styrene ionomers, blends were prepared as for the acrylate ionomers. However the high temperatures necessary for drying the styrene ionomers may have caused some decomposition of the PEI. In any case, the DM behaviour of these blends was quite different from that of the acrylate polymers: the matrix

peak was moved to lower temperatures (typically 20°C for 20 wt % PEI) and no cluster peak was observed.

Blends of sulfonated polyphenylenes with ethylacrylate-4-vinylpyridine copolymers containing different levels of interacting groups were prepared. For equivalent weights of 600 and below, a single broad descent in the storage modulus was observed in the dynamic mechanical studies. While the breadth of the drop in G' with T suggests that the mixture is heterogeneous, the absence of two well defined steps in G' vs T plot indicates that these blends exhibit the effects of strong interactions due to the presence of the ionic groups. Miscibility enhancement was improved further by increasing the concentration of the interacting groups in the polymers. Proton transfer was confirmed by Fourier transform Infrared Spectroscopy (FT-IR), which revealed the presence of a new peak due to the vinylpyridinium ion (VPH^+) at 1640 cm^{-1} . The extent of proton transfer was ca. 80% for equivalent weights of 600 and below.

The high and low cohesive energy density polymer blends were prepared by blending Nafion and ethylacrylate-4-vinylpyridine copolymers. Miscibility enhancement was found for blend samples prepared at 250°C from 1% DMF. The dynamic mechanical studies show that the glass transition

temperatures due ethylacrylate copolymers were shifted to higher temperatures for the miscible blend. This suggests that the polymer-polymer miscibility was achieved even in the case of Nafion and ethylacrylate-4-vinylpyridine blend via ionic interactions.

Poly(methyl methacrylate (MMA) and poly(styrene (S)) form immiscible blends. However, copolymers of MMA with 4-vinylpyridine (4VP) are miscible with sulfonated poly(S) because of proton transfer and the resulting ionic interaction. Both the proton transfer from the styrenesulfonic acid (SSA) group to the 4VP ring and the alignment of the chains that results from ion pair formation can be followed by NMR spectroscopy in dimethyl sulfoxide solutions at 85°C. The proton transfer takes place very quickly. The process of coil overlap is demonstrated by the upfield shift of all poly(MMS-co-4VP) signals induced by the aromatic shielding effect of the poly(S-co-SSA) units. For a comonomer content of 11 mol %, the process is completed in ca. 2h. One- and two-dimensional NOE-correlated spectra demonstrate the presence of dipolar coupling through space between the methoxy protons of poly(MMA-co-4VP) and the aromatic protons of poly(S-co-SSA). This indicates an interchain distance of about 4 Å (16).

B. Block Copolymers (17)

The progress in the ABA block copolymers has centered on three major areas. The first of these was a redesign of part of the vacuum line needed for the synthesis of the materials. It was found that if the vinyl-pyridine (VP) for the end blocks was added in bulk to the living polymerization mixture, a small number of very long end-blocks were formed, while some styrene chains remained uninvolved. The reason for this phenomenon was that the rate of polymerization of vinylpyridine is faster than the rate of initiation by the end capped styrene chains, so that VP chains, once formed, polymerize more rapidly than new chains are initiated. This leads to a very heterogeneous distribution of end block lengths. This problem was solved by designing a dilution burette which allows for the dilution of the vinylpyridine by a factor of 100 with the THF, and this modification solved the problem.

The second major aspect of the progress was the development of a method of quaternization of the ABA block copolymers. It was found that if attempts were made to quaternize the materials in solution, the solvents that have been used for the quaternization procedure lead to a precipitation of the partly quaternized product. Thus, it

was difficult to obtain fully quaternized materials or, in some cases, even homogeneous samples. To overcome this problem, a method was developed which involved the molding of an unquaternized sample and the subsequent swelling of this molded sample in a ethanol methyl iodide mixture. The ratio of ethanol to methyl iodide was adjusted to yield minimum swelling consistent with a reasonably rapid rate of quaternization. Also, at low methyl iodide levels, only a light swelling of the sample took place, which means that the dimensions of the sample were retained after desorption of the solvent. This procedure was found satisfactory for all the samples studied to date.

The final aspect of progress involved the study of the dynamic mechanical properties. Because of the low dequaternization temperature of vinylpyridinium methyl iodide, the samples of the quaternized block copolymers could not be dried at excessively high temperatures. Unfortunately, at the low temperatures used, a certain amount of water or other solvents remained in the quaternized regions. Naturally, the materials are phase separated, as are most ABA block copolymers of such dissimilar character. It was found that the glass transition temperature of the polystyrene, as expected,

remained approximately the same as that of the homopolymer. By contrast, the glass transition temperature of the ionic regions, which was expected to be very high, was found a relatively low values, sometimes even below the glass transition temperature of the polystyrene, because of the presence of residual solvent. As might be expected, the position of the low temperature glass transition of the ionic regions varied depending on the detailed drying conditions. The dynamic mechanical properties of the ionomeric blocks were also found to vary depending on the detailed methods of preparation. For example, if polymers prepared as outlined above were compared with block copolymers which had been reprecipitated from DMF in which the ionomer blocks are soluble, it was found that the equilibrium modulus changed by as much as one order of magnitude in the 9% sample. This is undoubtedly due to a dramatic change in the morphology of the phase separated ionic regions, and is true only for the 9% sample. By contrast, the 2, 5 and 7% samples showed identical behaviour independent of whether the sample was quaternized in situ, as described above, or whether it was reprecipitated after quaternization.

C. Structure-Property Relations

A major study was undertaken on the melt rheology of various ionomers and ionomer-plasticizer systems (18-20). The study was motivated, in part, by the realization that any applications involving the injection molding of ionomers would require melt rheology data, as well as by the intrinsic interest in the field. An earlier study dealt with the melt rheology of styrene-sodium methacrylate copolymers (21).

In the first phase of the present investigation, the dynamic melt rheology of random copolymers of polystyrene with 2-9 mol % 4-vinylpyridine were examined in their quaternized and non-quaternized forms. Time-temperature reducibility applied in all cases. Relative to the glass transition, the master curves of the non-quaternized materials were identical. Melt flow in the quaternized materials was mildly retarded, the extent increasing with ion content. At the highest ion contents, the relaxation processes appeared to be of the Arrhenius type. As in the glass transition regions, the ionic interactions in the plateau and terminal zones were thermally labile.

Another aspect of the study involved the investigation of plasticized ionomers. In this case, a high molecular

weight styrene ionomer containing 5 mol % sodium methacrylate was blended with a styrene oligomer (M.W. 800) and investigated using dynamic mechanical techniques. The focus of the study was on the dynamic melt rheology of these materials, whose ratios by weight of ionomer to oligomer were 60/40, 40/60 and 25/75. The glass transition temperature and ionic transition were first characterized by torsion pendulum measurements as a function of temperature. It appeared that a maximum level of plasticization was achieved for the ionic regions, the extent depending on sample history. Time-temperature superposition was obeyed by the blend of 60 wt % ionomer, but not by the other two blends. Relaxations due to the ionic regions were clearly evident in the relaxation spectra of all three blends. Above a certain temperature, the 25 wt % blend indicated an Arrhenius type of temperature dependence.

Other plasticizers were also explored for the styrene ionomers. In this investigation, the plasticizer effect of a nonpolar and a polar diluent in ionomers was studied by dynamic mechanical methods in the glassy to rubbery regions. Specifically, a carboxylate and a sulfonate polystyrene-based ionomer were investigated as a function of diethylbenzene (DEB) content and of glycerol content. It

was found that the nonpolar diluent plasticizes the transition due to ionic aggregates as well as the glass transition. However, the ionic regions of the carboxylate ionomer were plasticized more than those of the sulfonate ionomer. This corroborates the results of other studies which had found that the sulfonate groups in ionomers interact more strongly than the carboxylate groups. The polar diluent caused the ionic transition to disappear; this was probably due to solvation of the ions by the diluent.

As a continuation of the investigation of different ionic groups, two studies were performed on materials containing the $-O^-Na^+$ moiety in polystyrene (22-24).

In the first of these, polystyrene-co-4-hydroxystyrene ionomers (3.0-22 mol %) were synthesized via neutralization of demethylated polystyrene-co-4-methoxystyrene. The physical properties of the ionomers as well as their nonionic precursors were studied by calorimetry, torsion pendulum and small-angle X-ray scattering (SAXS). Evidence for ion aggregation was obtained for the styrene-4-hydroxystyrene ionomers from SAXS and torsion pendulum studies. By comparison with other anionic ionomers, it was found that the degree of perturbation by the clusters was low, but that they were definitely present.

In a second study, the effect of the introduction of a methylene group between the ring and the ion was investigated. Polystyrene-co-4-hydroxymethylstyrene ionomers (2.5-19.4 mol %) were prepared from the partial chloromethylation of polystyrene, followed by esterification, saponification and finally neutralization. SAXS and torsion pendulum studies show no evidence of extensive clustering. The small multiplets, which are present, persist to very high temperatures, and make the material behave like a crosslinked system. The presence of the methylene group between the ring and the ionic moiety is thus seen to influence the properties appreciably.

Finally, an extensive study was undertaken to explore the effect of changes in the dielectric constant, the ion structure, and the glass transition temperature on cluster formation as opposed to multiplet formation (25). The investigation of the dynamic mechanical properties of ethyl acrylate-sodium acrylate ionomers and a comparison of the results with those of styrene-based systems has confirmed the notion that as the matrix polarity increases, the extent of clustering decreases. As a consequence, the value of the critical concentration above which the clusters dominate the general behavior increases with the dielectric constant of

the matrix. Ultimately, the multiplet solubility limit could be infinite and cluster formation impossible if the matrix dielectric constant were very high. This had, indeed, been observed in the phosphates (26). While poly(ethyl acrylate-sodium acrylate) ionomers are undoubtedly phase-separated, the poly(ethyl acrylate-co-4-vinyl pyridine quaternized) (4VPQ) and poly(ethyl acrylate-co-2-methyl-5-vinyl pyridine quaternized) (2Me5VPQ) ionomers are homogeneous materials. This is most probably due to the fact that the coulombic interactions between the large-size vinylpyridinium iodide ions are too weak to allow the formation of clusters. Hence, only multiplets are present. The latter were shown to act as reversible thermolabile crosslinks which do not exert much influence above the glass transition temperature. This is consistent with the stress relaxation results obtained for samples of high ion content. The thermolabile crosslinks affect the glass transition temperature to the same extent as covalent crosslinks. This result parallels that found in the poly(styrene-4-vinyl pyridine) ionomers.

Quite unexpectedly, the structure of the ionic moieties (4-VPQ, 2-Me-5-VPQ) seems to influence multiplet formation, at least at low ion content. A small but finite

ion concentration is needed in the latter case before multiplet formation is detected, while no such threshold concentration is observed in the case of 4-VPQ.

In a subsequent investigation, an attempt was made to see how the glass transition temperature affected multiplet formation. It was found that the matrix glass transition temperature has little influence on multiplet formation for materials with T_g 's above -20°C , since the EA and MMA ionomers with 4-VPQ and 2-Me-5-VPQ ions, which have matrix glass transition temperatures 150°C apart, behave in the same manner. The vinylpyridinium ions act as thermolabile ionic crosslinks. This factor alone is sufficient in explaining the rise in glass transition temperature, since the ionic crosslinks are as efficient as covalent crosslinks in raising the glass transition temperature. The results confirmed the previous finding that the structure of the ion itself is a factor that has to be considered when investigating the bulk properties of ionomers, since shielding of the charge inhibits multiplet formation.

Finally it was shown that if the glass transition is depressed considerably below -20°C , clustering can indeed, take place. Thus, the BuA-4-VPQ ionomers were shown to be clustered materials. In addition, the investigation of the

viscoelastic properties of EA-4-VPQ 10.5 mol % samples plasticized with dimethylmalonate has univocally demonstrated that the essential condition for vinylpyridinium ions to form clusters is a very low matrix glass transition temperature. This agrees with the suggestion that cluster decomposition in low glass transition temperature vinylpyridinium ionomers of low dielectric constant (butadiene) occurs at about 20°C (27).

In the light of these results, it now seems surprising that the low concentration (<10 mol %) EA-4-VPQ ionomers did not show any sign of phase separation. These have a glass transition temperature below the cluster decomposition temperature mentioned above. Thus, it appears that these materials are a border line case, and would probably be clustered if their glass transition temperatures or dielectric constant were slightly lower.

Proton and carbon NMR spectra in solution of poly(methyl methacrylate - co - 4-vinyl pyridine), poly(methyl methacrylate - co - 2-methyl-5-vinyl pyridine) and of their derivatives obtained by quaternization with methyl iodide are presented. The vinyl pyridine structural units content of the samples is of ca. 10%. In different solvents, the spectra provide information about the sequence

distribution and configuration of the copolymers. A "coisotactic" alternating addition, defined as the probability to find a methoxy group and a pyridine ring neighbouring each other on the same side of the main chain, can be estimated to be about 0.5 in both cases. This information arises from the splitting of the aromatic and of the methoxy signals (both in proton and carbon spectra). As expected, quaternization does not affect the copolymer configuration. Heteronuclear correlated two-dimensional spectra can help in assigning the spectra (28).

The glass transition temperature (T_g) and dynamic mechanical properties of random copolymers of styrene-4-vinylpyridine quaternized with iodoalkanes were studied for vinylpyridine contents up to ten percent and pendant alkyl chains up to ten carbons in length. Two linear relationships, between ion content and glass transition temperature and between pendant alkyl chain length and the T_g , were observed. An equation was proposed that can be used to predict the T_g for such copolymers based on their ion contents and alkyl chain lengths (29).

The effect of internal plasticization on clustering in a carboxylated styrene-based ionomer was investigated. A copolymer of styrene with methacrylic acid (7 mol %) was

alkylated with 1-decene in a Friedel-Crafts type of reaction. Both glass transition temperatures (T_g 's), associated to the matrix and the clusters, were shifted down with increasing alkylation levels, and the modulus at the rubber-like inflection point dropped by over an order of magnitude. The evaluation of the apparent average molecular weight between crosslinks (M_c) showed that at the higher alkylation levels, ionic association was mainly limited to multiplets. The large drop in the rubber-like modulus showed that even though ionic clustering effects were still observed in the loss tangent-temperature curves, their influence on the rheological properties of the polymer were not significant.

Three-armed ionically terminated "stars" were used to determine the kinetics of ion-hopping or interchange. These species form a network in which the ionic aggregates provide the weak links. Stress relaxation techniques were utilized, and from the relaxation times the kinetic parameters were calculated. For the sodium sulfonate terminal groups, the first order rate constant is given by $k = 7.11 \times 10^9 \exp(-94,000/RT)$ with ΔH in Joules/mol. (30).

D. Membranes

Until the fall of 1985, the membrane research was

supported by a contract with NRC Canada, which was in effect for ca. 7 years. The work covered the casting of very high T_g completely aromatic ionomer membranes, and the study of their mechanical properties, both dry and immersed in water or aqueous alkali. The materials were obtained as a result of a collaboration with Professor F. Harris of the University of Akron. Since the fall of 1985, the person working on this project has been paid out of ARO funds; this ARO contract thus receives the benefit of considerable accumulated experience with this new class of membrane materials.

Recent work has centered on the characterisation of carboxylated or sulfonated phenylated phenylenes, ranging in degree of substitution all the way from the nonionic material down to an equivalent weight of ca. 600. Spectroscopic (FT-IR), thermal (DSC) and mechanical (dynamic mechanical, ~1 Hz) techniques have been used. Differential scanning calorimetric studies of the carboxylated ionomers show a transition at high temperature, in addition to one at ca. 290°C. The high temperature transition moves to higher temperature with increasing ionic content and may be related to ionic aggregates. Torsion pendulum results showed a significant increase in the glass transition temperature of

the ionomer relative to that of its ester precursor (namely from 290°C to 440°C), but gave no evidence of ionic clustering. Stress-strain studies performed both in water and in 20% KOH solution at 80°C indicated that the mechanical properties of the material remain stable under these conditions. The behavior of these ionomers at high temperature and in an alkaline solution suggests a possible use of these films as separators in an alkaline electrolysis cell.

Studies on the sulfonated aromatic ionomers also show a dramatic increase in the glass transition temperature due to the presence of ionic crosslinks.

In addition to the above studies, the materials were also incorporated in blends (see above). The unblended materials show promise in high temperature separator applications, such as batteries or electrolyzers.

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